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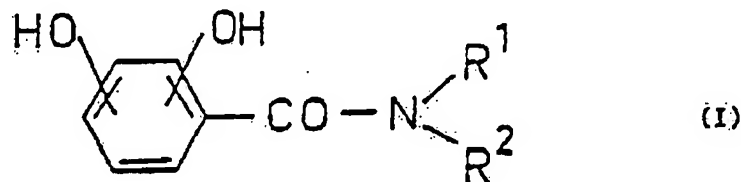
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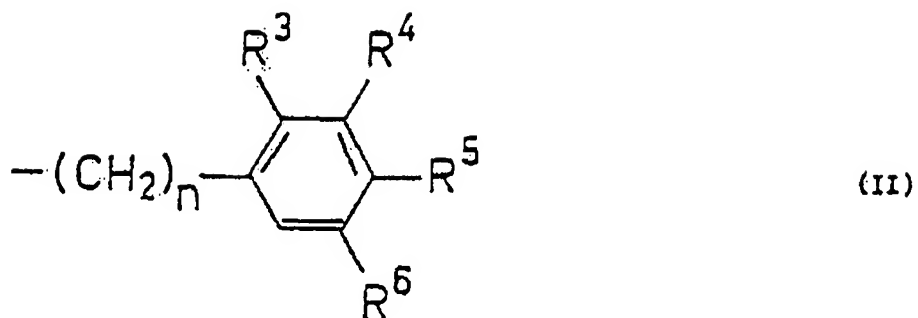
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(54) **Oxidation hair colouring agents**

- 5 (57) Hair colouring agents containing oxidation colorant intermediate products with usual developer components in a cosmetic support which contain as coupler components dihydroxybenzamides of the general formula I



- 10 in which R¹ and R² independent of one another represent hydrogen or alkyl groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups [sic], each with 2 – 4 carbon atoms, pyridyl groups or groups of the formula (II)



5 wherein n is = 0 – 4 and R³ – R⁶ stand for hydrogen or hydroxyl groups, alkyl
 or alkoxy groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups,
 each with 2 – 4 carbon atoms, for NR⁷R⁸ groups, with R⁷ and R⁸ for hydrogen,
 or alkyl groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups,
 each with 2 – 4 carbon atoms, or for the carboxyl groups, wherein at least two
 10 of the radicals R³ – R⁶ are hydrogen atoms and no more than one radical is a
 carboxyl group, are marked by a high light and cold wave fastness of the hair
 colorants formed and the improved levelling thereof, i.e. the very uniform
 distribution thereof on the hair from the hairline to the end of the hair.

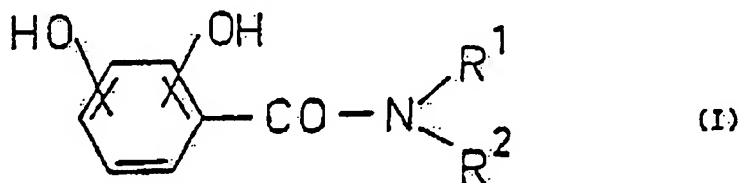
Oxidation hair colorants with new couplers

The object of the invention are hair colouring agents based on oxidation colorants. Such hair colouring agents contain oxidation colorant intermediate products in a cosmetic support. Developer substances and coupler substances which under the influence of oxidising agents or of atmospheric oxygen form colorants are used as oxidation colorant intermediate products. Creams, emulsions, gels, shampoos, foam aerosols or other preparations which are suitable for application to the hair serve as cosmetic supports for the oxidation colorant intermediate products.

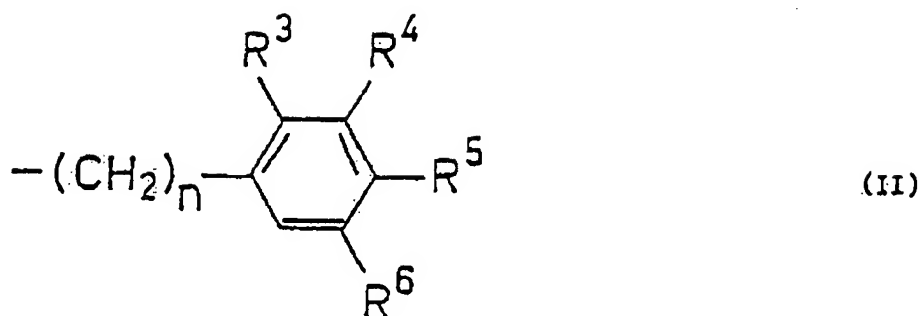
The so-called oxidation colourings which are produced by oxidative coupling of one or several developer components with one another or with one or several coupler components, play a preferred role for colouring hair due to their intensive colourings and good fastness properties. Usually primary aromatic amines with a further free or substituted hydroxy or amino group situated in para or ortho position, furthermore diaminopyridine derivatives, heterocyclic hydrazone derivatives, 4-aminopyrazolone derivatives and tetraaminopyrimidines are used as developer substances. m-Phenylenediamine derivatives, naphthols, resorcinol derivatives and pyrazolones are used as coupler substances.

Good oxidation hair colorant intermediate products must primarily fulfil the following requirements: They must form the desired colour shades in sufficient intensity during oxidative coupling. They must furthermore possess a good absorptive capacity on human hair without colouring the scalp too strongly. The colourings produced in this way must exhibit a high stability to abrasion, heat, light and the chemicals used in perming the hair. Finally the oxidation hair colorant intermediate products should be toxicologically and dermatologically harmless.

It was then found that hair colouring agents containing oxidation colorant intermediate products with usual developer components in a cosmetic support which contain as coupler components dihydroxybenzamides of the general formula (I)



in which R^1 and R^2 independent of one another represent hydrogen or alkyl groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups, each with 2 – 4 carbon atoms, pyridyl groups or groups of the formula (II)



5 wherein n is = 0 – 4 and R³ – R⁶ stand for hydrogen or hydroxyl groups, alkyl
 or alkoxy groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups,
 10 each with 2 – 4 carbon atoms, for NR⁷R⁸ groups, with R⁷ and R⁸ for hydrogen,
 or alkyl with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl, each with 2 – 4
 carbon atoms, or for the carboxyl group, wherein at least two of the radicals
 R³ – R⁶ are hydrogen atoms and no more than one radical is a carboxyl
 group, satisfy these requirements to a high degree. In particular the hair
 colorants formed are marked by a high light and cold wave fastness and by an
 improved levelling, i.e. a very uniform distribution on the hair from hairline to
 the end of the hair.

15 The coupler components according to the invention are already
 described in the literature, for example in German Offenlegungsschrift 27 10
 653, German Auslegeschrift 10 64 074, European Patent Application 161 655,
 British Patent Specification 872 683, French Patent Specification 1 571 198
 and Belgian Patent Specification 813 815. They can be produced in principle
 by reacting dihydroxybenzoic acid in the form of the acid chloride in which the
 hydroxy groups are acetylated, with the corresponding amines. A
 20 corresponding work specification can be found for example in German
 Auslegeschrift 10 64 074.

Of the dihydroxybenzamides described by formula (I), the 2,4-
 dihydroxybenzamides are preferred.

25 It is furthermore preferred using such dihydroxybenzamides of the
 general structure (I) in which R¹ stands for a hydrogen atom. In the
 framework of these named substances, it is in turn preferred using those
 compounds in which R² stands for hydrogen, a methyl group, a pyridyl group
 or a group of the formula (II), wherein R³ – R⁶ stand for hydrogen, methoxy
 groups, amino groups, N,N-dimethylamino groups or the carboxyl group,
 30 wherein at least two of the groups R³ – R⁶ are hydrogen atoms and no more
 than one group is a carboxyl group.

35 The dihydroxybenzamides are used in the hair colouring agents
 according to the invention preferably in free form; the corresponding salts can
 however also be used if acid or basic groups are contained. The compounds
 with a –COOH- group can for instance be used in the form of the alkali or
 ammonium salts, compounds with amine groups for example also in the form
 of the hydrochlorides.

40 Particularly suitable coupling components are N-phenyl-2,4-
 dihydroxybenzamide, N-(2'-methoxyphenyl)-2,4-dihydroxybenzamide, N-(3'-
 methoxyphenyl)-2,4-dihydroxybenzamide, N-(4'-methoxyphenyl)-2,4-

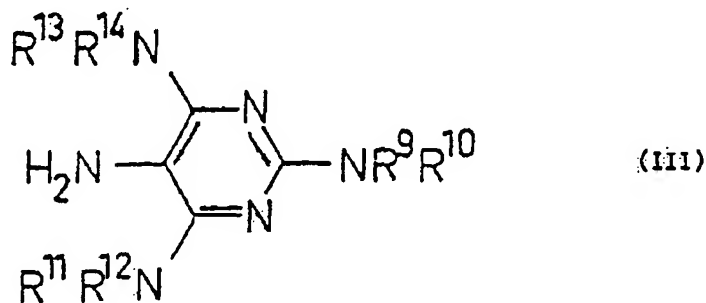
dihydroxybenzamide, N-(4'-carboxyphenyl)-2,4-dihydroxybenzamide, N-(2'-pyridyl)-2,4-dihydroxybenzamide, N-(3'-pyridyl)-2,4-dihydroxybenzamide, N-(2',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide, N-(3',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide, N-(2'-methoxy-5'-amino-phenyl)-2,4-dihydroxybenzamide, N-(4'-N,N,-dimethylamino)phenyl)-2,4-dihydroxybenzamide, N-(4'-hydroxyphenyl)-2,4-dihydroxybenzamide, N-methyl-2,4-dihydroxybenzamide, N-benzyl-2,4-dihydroxybenzamide and the unsubstituted 2,4-dihydroxybenzamide.

The hair colouring agents according to the invention can, apart from the dihydroxybenzamides of the general formula (I), also contain other known coupler substances which are necessary to modify the colour shades and to produce natural tints. Such usual coupler compounds are e.g. other m-phenylenediamines, e.g. 2,4-diaminophenyl-2-hydroxyethyl ethers, or N-(2,4-dihydroxybenzylidene)-amino compounds, phenols, resorcinols, m-aminophenols, naphthols or pyrazolones.

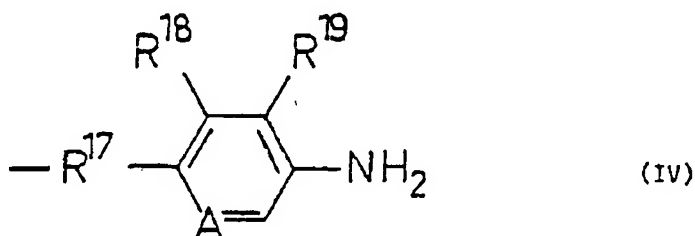
Optionally direct colorants can also be used in addition to further modify the colour shades. Such direct colorants are e.g. nitrophenylenediamines, nitroaminophenols, anthraquinone colorants or indophenols.

In the hair colouring agents according to the invention, e.g. aromatic amines with one or several other NH₂ groups, NHR groups or NR₂ groups, wherein R is an alkyl group with 1 – 4 C atoms or a hydroxyalkyl group or an aminoalkyl group with 2 – 4 C atoms, amino phenols, aminophenol ethers and/or diaminopyridine derivatives can be used as developer substances. Such developer substances are e.g. p-phenylenediamine, p-toluylenediamine, N-methyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N-hydroxyethyl-p-phenylenediamine, N,N-bis(2-hydroxyethyl)p-phenylenediamine, N-ethyl-N-(2-hydroxyethyl)p-phenylenediamine, N,N-diethyl-2-methyl-p-phenylenediamine, 2-chloro-p-phenylenediamine, 2,6-dichloro-p-phenylenediamine, 2-chloro-6-methyl-p-phenylenediamine, 2-methoxy-p-phenylenediamine, 2,5-diaminoanisole, 6-methoxy-3-methyl-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine, N-(2-hydroxypropyl)-p-phenylenediamine, N-butyl-N-sulphobutyl-p-phenylene diamine, N-(p-aminophenyl)-N,N'-bis-(β-hydroxyethyl)-1,3-diaminopropane or the salts thereof with inorganic or organic acids.

Particularly suitable developer substances for the coupler components according to the invention are 2,4,5,6-tetraaminopyrimidines of the general formula (III),



- in which $R^9 - R^{14}$ can mean hydrogen, an alkyl radical with 1 – 4 carbon atoms, the radical $-(CH_2)_m-X$ in which $m = 1 - 4$ and X a hydroxyl group, a halogen atom, a $-NR^{15}R^{16}$ group, wherein R^{15} and R^{16} can mean hydrogen or alkyl radicals with 1 – 4 carbon atoms, or an optionally substituted aryl radical, or on condition that $R^{11} - R^{14}$ are hydrogen atoms, $-NR^9R^{10}$ stands for a group (IV)



- in which R^{17} is a group $-NH-(CH_2)_p-NH-$, wherein $p = 2 - 4$, a group $-NH-CH_2-CH(OH)-CH_2-NH-$ or a group



- R^{18} and R^{19} independent of one another are hydrogen, chlorine or a group $-OR^{20}$, wherein R^{20} is an alkyl group with 1 to 4 C atoms and A is a CH group or a nitrogen atom, or R^9 and R^{10} and/or R^{11} and R^{12} and/or R^{13} and R^{14} can form with the relevant nitrogen atom a heterocyclic, 5- or 6-member ring with one or two nitrogen atoms or a nitrogen and an oxygen atom, and the salts thereof with inorganic or organic acids.

- Suitable substances from this compound class are e.g. 4,5-diamino-2,6-bis-methylaminopyrimidine, 2,5-diamino-4-diethylamino-6-methylaminopyrimidine, 2,4,5-triamino-6-anilino-pyrimidine, 2,4,5-triamino-6-morpholino-pyrimidine and 2,4,5-triamino-6-(2-hydroxyethyl)-aminopyrimidine.

- Quite particularly suitable as developer component is the unsubstituted 2,4,5,6-tetraaminopyrimidine.

- It is not necessary for the compounds of formula (I) according to the invention and the oxidation colorant intermediate products otherwise present in the hair colouring agents or direct colorants to be uniform chemical compounds. Rather these can also be mixtures of the coupler or developer substances to be used according to the invention.

- Compounds of the formula (I) and the optionally additionally present known coupler substances are applied to the hair colouring agents according to the invention in general in approximately molar quantities based on the developer substances used. If the molar charge has also proved suitable, then a certain excess of individual oxidation colorant intermediate products is not unfavourable, so that developer substances and coupler substances can be contained in a molar ratio of 1: 0.5 to 1: 2.

- The oxidative development of the colouring can in principle take place with atmospheric oxygen. A chemical oxidant however is preferably used particularly when in addition to the colouring a brightening effect on the hair is

Table I

Amine used	Dihydroxybenzamide according to formula I	Melting point (°C)
Aniline	N-phenyl-2,4-dihydroxybenzamide · 0.5 H ₂ O	142
2-Methoxyaniline	N-(2'-methoxyphenyl)-2,4-dihydroxybenzamide · 2 H ₂ O	60 - 65
3-Methoxyaniline	N-(3'-methoxyphenyl)-2,4-dihydroxybenzamide · H ₂ O	115 - 120
4-Methoxyaniline	N-(4'-methoxyphenyl)-2,4-dihydroxybenzamide	209 - 210
4-Aminobenzoic acid	N-(4'-carboxyphenyl)-2,4-dihydroxybenzamide · 0.5 H ₂ O	> 250
2-Aminopyridine	N-(2'-pyridyl)-2,4-dihydroxybenzamide · 1.5 H ₂ O	210 - 230
3-Aminopyridine	N-(3'-pyridyl)-2,4-dihydroxybenzamide · 0.5 H ₂ O	> 250
2,5-Dimethoxyaniline	N-(2',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide · 2 H ₂ O	135 - 136
3,5-Dimethoxyaniline	N-(3',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide · 2.5 H ₂ O	165 - 166
2-Methoxy-5-aminoaniline	N-(2'-methoxy-5'-amino-phenyl)-2,4-dihydroxybenzamide · H ₂ O	230 - 235 (Z)
4-N,N-dimethylaminoaniline	N-(4'-(N,N-dimethylamino)phenyl)-2,4-dihydroxybenzamide · 3 H ₂ O	252 (Z)
4-Aminophenol	N-(4'-hydroxyphenyl)-2,4-dihydroxybenzamide · H ₂ O	228 - 230 (Z)
Methylamine	N-methyl-2,4-dihydroxybenzamide	188 - 190
Benzylamine	N-benzyl-2,4-dihydroxybenzamide · 0.5 H ₂ O	84 - 85

Table 1 contd.

Amine used	Dihydroxybenzamide according to formula I	Melting point (°C)
Aniline	N-phenyl-3,5-dihydroxybenzamide	112 - 114
Aniline	N-phenyl-2,5-dihydroxybenzamide · 0.5 H ₂ O	190 - 192
Aniline	N-phenyl-2,6-dihydroxybenzamide	200 - 205
Ammonia	2,4-dihydroxybenzamide · 0.5 H ₂ O	220 (Z)
N-Methylaniline	N-methyl-N-phenyl-2,4-dihydroxybenzamide · H ₂ O	140 - 143
N-Methyl-4-methoxyaniline	N-methyl-N-(4'-methoxyphenyl)-2,4-dihydroxybenzamide	148 - 150
3-Aminophenol	N-(3'-hydroxyphenyl)-2,6-dihydroxybenzamide · 0.5 H ₂ O	230 - 236 (Z)
4-Aminophenol	N-(4'-hydroxyphenyl)-2,6-dihydroxybenzamide	230 - 235 (Z)

II. Application tests

Hair colouring agents according to the invention were produced in the form of a hair colorant cream emulsion of the following composition:

Fatty alcohol C ₁₂ – C ₁₄	10.0 g
Fatty alcohol C ₁₂ – C ₁₄ + ethylene oxide sulphate, Na salt, 28%	25.0 g
Water	60.0 g
2,4,5,6-tetraaminopyrimidine	7.5 mMol
Coupler component	7.5 mMol
Na ₂ SO ₃ (inhibitor)	1.0 g
Concentrated ammonia solution	up to pH = 9.5
Water	ad 100 g

The constituents were mixed together in order. After addition of the oxidation colouring agent intermediate products and the inhibitor, the pH of the emulsion was at first set at 9.5 with concentrated ammonia solution, then made up to 100 g with water.

The oxidative development of the colouring was carried out with 3% hydrogen peroxide solution as oxidising agent. 100 g of the emulsion were added to 50 g hydrogen peroxide solution (3%) and mixed.

The colouring cream was standardised on approx. 5 cm long strands, applied to 90% greyed but not specially pre-treated human hair and left there for 30 minutes at 27°C. When the colouring process was complete, the hair was rinsed, washed out with a usual shampoo and then dried. The colour shades of the coloured strands of hair obtained with the named oxidation colouring agent intermediate products are shown in Table 2.

Table 2

Coupler component	Colour shade
N-phenyl-2,4-dihydroxybenzamide	Purplish brown
N-(2'-methoxyphenyl)-2,4-dihydroxybenzamide	Purplish blue
N-(3'-methoxyphenyl)-2,4-dihydroxybenzamide	Dark ruby
N-(4'-methoxyphenyl)-2,4-dihydroxybenzamide	Bluish purple
N-(4'-carboxyphenyl)-2,4-dihydroxybenzamide	Reddish brown
N-(2'-pyridyl)-2,4-dihydroxybenzamide	Reddish brown
N-(3'-pyridyl)-2,4-dihydroxybenzamide	Reddish brown
N-(2',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide	Bluish purple
N-(3',5'-dimethoxyphenyl)-2,4-dihydroxybenzamide	Bluish purple
N-(2'-methoxy-5-amino-phenyl)-2,4-dihydroxybenzamide	Blackish purple
N-(4'-(N,N-dimethylamino)phenyl)-2,4-dihydroxybenzamide	Purple
N-(4'-hydroxyphenyl)-2,4-dihydroxybenzamide	Bluish purple
N-methyl-2,4-dihydroxybenzamide	Red
N-benzyl-2,4-dihydroxybenzamide	Purplish brown
2,4-dihydroxybenzamide	Orange-brown

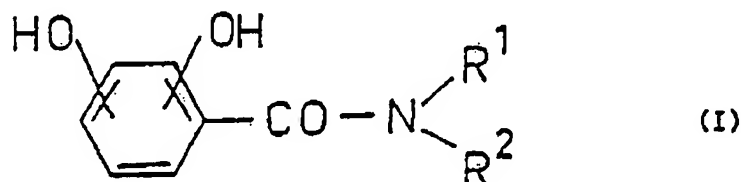
Table 2 contd.

Coupler component	
N-methyl-N-phenyl-2,4-dihydroxybenzamide	Greyish purple
N-methyl-N-(4'-methoxyphenyl)-2,4-dihydroxybenzamide	Greyish red
N-phenyl-3,5-dihydroxybenzamide	Purplish brown
N-phenyl-2,5-dihydroxybenzamide	Purplish brown
N-phenyl-2,6-dihydroxybenzamide	Brown *
N-(3'-hydroxyphenyl)-2,6-dihydroxybenzamide	Brown
N-(4'-hydroxyphenyl)-2,6-dihydroxybenzamide	Brown

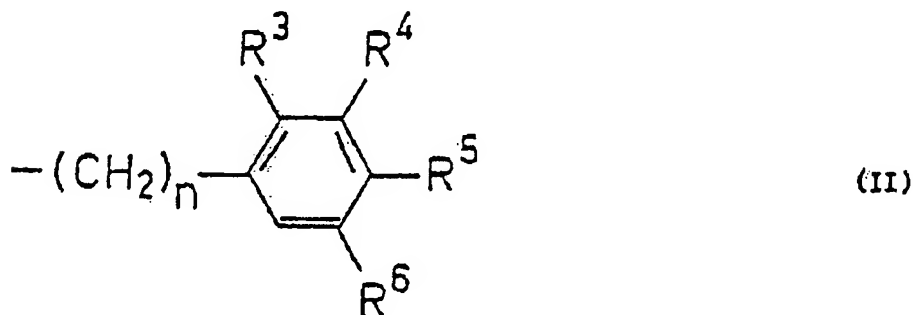
* = with p-toluylenediamine as developer component

Claims

1. Hair colouring agents containing oxidation colorant intermediate products with usual developer components in a cosmetic support, characterised in that they contain as coupler components dihydroxybenzamides of the general formula (I)



in which R^1 and R^2 independent of one another represent hydrogen or alkyl group with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups [sic], each with 2 – 4 carbon atoms, pyridyl groups or groups of the formula (II)

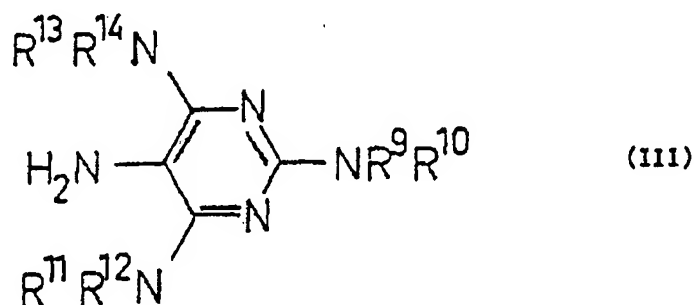


wherein n is $= 0 - 4$ and $\text{R}^3 - \text{R}^6$ stand for hydrogen or hydroxyl groups, alkyl or alkoxy groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups, each with 2 – 4 carbon atoms, for NR^7R^8 groups, with R^7 and R^8 for hydrogen, or alkyl groups with 1 – 4 carbon atoms, hydroxyalkyl or aminoalkyl groups, each with 2 – 4 carbon atoms, or for the carboxyl group, wherein at least two of the radicals $\text{R}^3 - \text{R}^6$ are hydrogen atoms and no more than one radical is a carboxyl group.

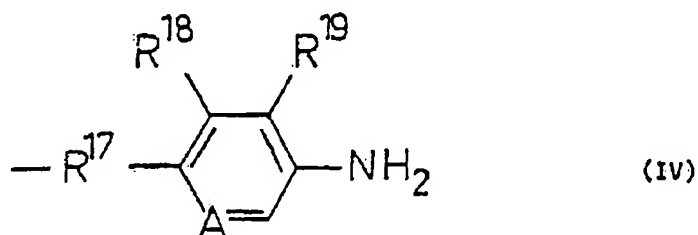
2. Hair colouring agents according to claim 1, characterised in that they contain as coupler components dihydroxybenzamides corresponding to the general formula (I) in which the hydroxyl groups stand in positions 2 and 4.

3. Hair colouring agents according to claim 1 or 2, characterised in that they contain as coupler components dihydroxybenzamides of the general formula (i) in which R^1 represent hydrogen and R^2 hydrogen, a methyl group, a pyridyl group or a phenyl group of the formula (II), wherein $\text{R}^3 - \text{R}^6$ stand for hydrogen or methoxy groups, amino groups, N,N-dimethylamino groups or the carboxyl group on condition that at least two of these groups $\text{R}^3 - \text{R}^6$ are hydrogen atoms and the molecule contains maximum one carboxyl group.

4. Hair colouring agents according to one of claims 1 to 3, characterised in that they contain as developer components 2,4,5,6-tetraaminopyrimidines of the general formula (III)



in which $\text{R}^9 - \text{R}^{14}$ represents hydrogen, an alkyl radical with 1 – 4 carbon atoms, the radical $-(\text{CH}_2)_m\text{-X}$, in which $m = 1 - 4$ and X a hydroxyl group, a halogen atom, a $-\text{NR}^{15}\text{R}^{16}$ group, wherein R^{15} and R^{16} can mean hydrogen or alkyl radical with 1 – 4 carbon atoms, or on condition that $\text{R}^{11} - \text{R}^{14}$ are hydrogen atoms, $-\text{NR}^9\text{R}^{10}$ stands for a group (IV)



in which R^{17} is a group $-\text{NH}-(\text{CH}_2)_p\text{-NH}-$, wherein $p = 2 - 4$, a group $-\text{NH}-\text{CH}_2\text{-CH}(\text{OH})-\text{CH}_2\text{-NH}-$ or a group



R^{18} and R^{19} independent of one another are hydrogen, chlorine or a group $-\text{OR}^{20}$, wherein R^{20} is an alkyl group with 1 to 4 C atoms and A is a CH group or a nitrogen atom, or R^9 and R^{10} and/or R^{11} and R^{12} and/or R^{13} and R^{14} can form with the relevant nitrogen atom a heterocyclic 5- or 6-member ring with one or two nitrogen atoms or a nitrogen and an oxygen atom, and/or the salts thereof with inorganic or organic acids.

5. Hair colouring agents according to one of claims 1 to 4, characterised in that they contain as developer component 2,4,5,6-tetraaminopyrimidine.

6. Hair colouring agents according to one of claims 1 to 5, characterised in that they contain 0.2 – 5 %w/w, in particular 1 – 3 %w/w, of oxidation colorant intermediate products.